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An Ionic Liquid-Mediated Route to Cerium(III) Bromide Solvates

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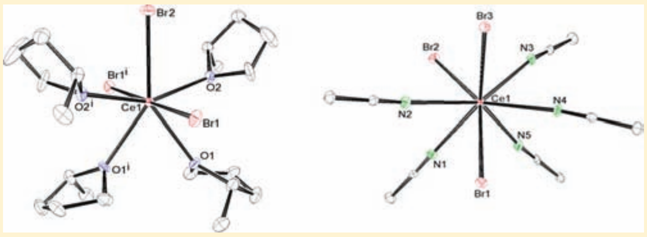
S *Supporting Information*

ABSTRACT: A novel synthetic route to a series of cerium bromide solvates is reported. The combination of bulk cerium bromide and the ionic liquid (IL) 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide results in a precursor paste that enhances the solubility of the cerium(III)bromide moiety in a number of donor solvents. Crystallization from these solvents has resulted in the isolation and characterization of $CeBr_3(THF)_4$ (**2**), $CeBr_3(2\text{-Me-THF})_4$ (**3**), and $CeBr_3(MeCN)_5 \cdot MeCN$ (**4**). Additionally, **2** is shown to be an efficient precursor for the new species $CeBr_3(py)_4$ (**5**) and $CeBr_3(bipy)(py)_3$ (**6**).



INTRODUCTION

The development of organolanthanide chemistry has been successful in large part due to the availability of solvated, hydrocarbon-soluble lanthanide halide precursors.[1] The oligomeric nature of many lanthanide trihalides results in extremely low solubilities in most organic solvents, somewhat limiting the utility of commercially available sources. As a consequence, much attention has been devoted to the development of synthetic routes to Lewis base adducts of these materials,[2] which are more amenable to dissolution in common organic solvents. While a number of routes exist to such species, examination of the Cambridge Crystallographic Database reveals that the vast majority of solvated lanthanide trihalides bear oxygen donor ligands,[3] suggesting a potential limitation to current methods. While the oxophilicity of the *f* elements is well established, the paucity of examples of lanthanide trihalides coordinated by other donor ligands is quite surprising.

Due to our interest in lanthanide containing scintillators, we became interested in developing a strategy for a mild, general synthesis of monomeric cerium(III) bromide ($CeBr_3$) fragments that would permit the incorporation of a broad spectrum of solvating ligands. $CeBr_3$ and $LaBr_3$:Ce are recently discovered materials that are among the best-performing of all known scintillators.[4] Rather than pursuing a bottom-up approach involving the formation of cerium-bromide bonds from multiple precursors, we opted to employ a top-down methodology beginning with commercially available bulk cerium bromide material. As recent studies have shown that ILs can play a vital role in ligand exchange processes of the *f* elements,[5] it seemed feasible that initial incorporation of an IL into our synthetic approaches may aid the conversion of a bulk lanthanide trihalide into a solvated molecular adduct.

The addition of the IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[BMP][N(Tf)_2]$) to bulk $CeBr_3$ resulted in a precursor paste ($CeBr_3$/IL) that proved to be soluble in several organic solvents. Subsequent crystallization techniques resulted in a number of variously ligated cerium bromide systems, including monomeric $CeBr_3(THF)_4$, which itself proved to be an efficient precursor for other molecular adducts.

The synthetic methodologies employed herein are expected to expand the current library of trivalent lanthanide halide synthons and potentially lead to new and improved applications in organolanthanide and lanthanide containing materials chemistry. Further, the ability to readily tune the supporting ligands may have implications in the area of radiation detection, where a number of lanthanide halide scintillators have already demonstrated promising results.[6]

EXPERIMENTAL SECTION

General Procedures. All syntheses and manipulations were carried out under argon by using standard Schlenk techniques or inside a Vacuum Atmospheres glovebox. Anhydrous solvents were purchased from either Sigma Aldrich or Acros and stored over molecular sieves. $CeBr_3$ and $LaBr_3$ (99.999%) were purchased from Sigma Aldrich and used without further purification. $[BMP][N(Tf)_2]$ was synthesized

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according to literature procedures,[7] and all reagents were purchased from Sigma Aldrich and used without further purification. Elemental Analysis was performed by Midwest Microlab, LLC and Atlantic Microlab, Inc. NMR spectra were recorded at ambient temperature on a Bruker AV-400 spectrometer. X-ray diffraction data were collected by mounting crystals under Paratone on glass fiber loops on a Bruker Apex II system fitted with an Oxford nitrogen cryostream. Structure solution and refinement against F^2 were performed using SHELX97.[8] FTIR data were collected using a Bruker Vertex 80 V FT-IR spectrometer equipped with an MVP-pro Attenuated Total Reflection (ATR) attachment with a diamond window at 4 cm^{-1} resolution.

Preparation of $CeBr_3$/IL (1). $CeBr_3$ (104.2 g, 0.274 mol) and IL (380 mL) were mixed together in a glovebox and briefly homogenized in a commercial blender. The mixture was introduced into a Netzsch MiniCer bead mill fitted with a peristaltic pump to allow for continuous flow (also housed in a glovebox). A Huber Nuevo Unistat 425 chiller was used to control the product temperature (<20 °C) during milling operations (mill speed was 1500 rpm, milled for ~8 h). The product material was then centrifuged with a Sorvall WX Ultra 80 ultracentrifuge at 40 000 rpm for ~3 h. After decanting off the supernatant, the resulting paste was ~40% v/v $CeBr_3$.

Preparation of $CeBr_3(THF)_4$ (2). THF (5 mL) was added to **1** (2.50 g) and the mixture stirred for 5 min. After permitting the undissolved solid to settle, the solution was filtered, and the resulting clear, colorless solution was stored at −35 °C for 2 days, affording a crop of colorless crystalline plates. The resulting crystals were washed with cold THF (5 mL) and dried under argon. The identity was confirmed by matching of the single crystal X-ray diffraction unit cell to the published structure.[9] Yield; 0.456 g. FTIR: C−O stretch of neat THF, 1070 cm^{-1}; **2**, 1018 cm^{-1}. Anal. Calcd. for $C_{16}H_{32}O_4CeBr_3$: C, 28.76; H, 4.83. Found: C, 28.45; H, 4.72.

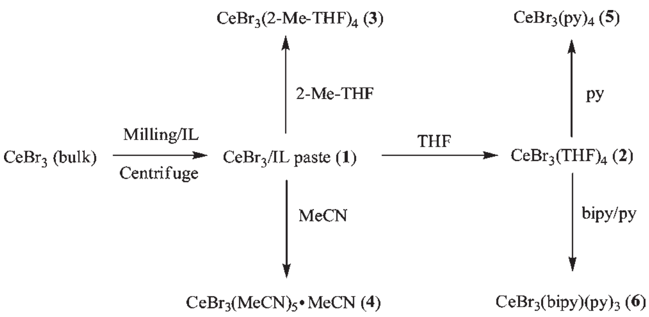
Note that upon stirring approximately 0.25 g of $CeBr_3$ in 10 mL of THF for 10 min (to make a saturated solution), filtering, and cooling of the solution to −35 °C in the glovebox freezer, only 34 mg of isolated product resulted.

Preparation of $CeBr_3(2\text{-Me-THF})_4$ (3). 2-Me-THF (5 mL) was added to **1** (1.00 g) and the mixture stirred for 5 min. The undissolved solid was permitted to settle and the solution decanted. Hexanes (1 mL) were added and the resulting solution filtered and stored at −35 °C for one week, resulting in the formation of colorless crystalline blocks. The crystals were washed with cold 2-Me-THF and dried under argon. Yield: 0.115 g. FTIR: C−O stretch of neat 2-Me-THF, 1065 cm^{-1}; **3**, 1057 cm^{-1}. Anal. Calcd. for $C_{20}H_{40}O_4CeBr_3$: C, 33.16; H, 5.57. Found: C, 20.71; H, 3.44; $CeBr_3[2\text{-Me-THF}]_{1.9}$.

Preparation of $CeBr_3(MeCN)_5 \cdot MeCN$ (4). Acetonitrile (5 mL) was added to **1** (2.50 g) and the mixture stirred for 5 min. After permitting the undissolved solid to settle, the solution was filtered, and the resulting clear, colorless solution was stored at −35 °C for 2 days, affording a large crop of colorless crystalline plates. The resulting plates were washed twice with cold acetonitrile (1 mL) and dried under argon. Yield: 0.420 g. After 30 min at ambient temperature, the crystals had changed to a white powder. FTIR: C≡N stretch of neat MeCN, 2254 cm^{-1}; **3**, 2273 cm^{-1}. Anal. Calcd. for $C_{12}H_{18}N_6CeBr_3$: C, 23.02; H, 2.88. Found: C, 13.55; H, 1.79; $CeBr_3[MeCN]_{2.8}$.

Preparation of $CeBr_3(py)_4$ (5). Pyridine (1 mL) was added to **2** (0.10 g, 0.15 mmol) and the clear solution stirred for 1 min. Toluene was added dropwise until the solution remained cloudy. The resulting solution was filtered and stored at room temperature for 2 days, resulting in a crop of large colorless needles. The crystals were filtered, washed with cold toluene, and dried in vacuo. Toluene was added to the mother liquor, and the crystallization process was repeated two more times. The combined crystalline crops were washed once more with cold toluene (1 mL) and dried in vacuo. Yield: 0.045 g, 51%. FTIR: C═C and C═N stretches neat pyridine, 1581 and 1439 cm^{-1}; **5**, 1599 and 1442 cm^{-1}.

Scheme 1. Synthetic Route to Cerium(III)bromide Solvates



Preparation of $CeBr_3(bipy)(py)_3$ (6). To a sample of **2** (0.050 g, 0.075 mmol) suspended in dichloromethane (10 mL) was added a solution of bipyridine (0.023 g, 0.150 mmol) in dichloromethane (3 mL) and the resulting yellow suspension stirred overnight. The reaction mixture was allowed to settle and the reaction solvent decanted. The yellow solid was washed twice with cold dichloromethane to remove unreacted bipyridine. The washed solid was dried in vacuo, resulting in the isolation of a bright yellow solid. Yellow crystalline blocks suitable for X-ray diffraction were grown by slow diffusion of hexanes into a saturated pyridine solution of the crude solid. The crystals were washed with cold toluene and dried under argon. Yield: 0.035 g, 62%. FTIR, C═C and C═N stretches: C═C and C═N stretches of neat pyridine, 1581 and 1439 cm^{-1}; **6** py, 1600 and 1441 cm^{-1}, **6** bipy, 1593 and 1436 cm^{-1}. Anal. Calcd for $C_{25}H_{23}N_5CeBr_3$: C, 38.83; H, 3.00; N, 9.06. Found: C, 37.71; H, 2.81; N, 8.58.

Preparation of $LaBr_3(THF)_4$ (7). $LaBr_3$ (0.50 g, 1.32 mmol) was added to THF (10 mL) and the mixture stirred at 55 °C for 30 min. The undissolved solid was permitted to settle out, and the solution was filtered. Storage of the resulting solution at room temperature for 2 h resulted in a crop of colorless, crystalline blocks. The crystals were isolated and dried under argon. Yield: 0.065 g. FTIR: C−O stretch of neat THF, 1070 cm^{-1}; **7**, 1018 cm^{-1}. Anal. Calcd for $C_{16}H_{32}O_4LaBr_3$: C, 28.81; H, 4.84. Found: C, 28.26; H, 4.75.

Preparation of $LaBr_3(MeCN)_5 \cdot 2MeCN$ (8). $LaBr_3$ (0.50 g, 1.32 mmol) was added to MeCN (10 mL) and the mixture stirred at 65 °C for 20 min. The undissolved solid was permitted to settle out, and the solution was filtered. After cooling to room temperature, the resulting solution was stored at −35 °C overnight, resulting in a crop of colorless, crystalline plates. The crystals were isolated and dried under argon. Yield: 0.100 g. FTIR: C≡N stretch of neat MeCN: 2254 cm^{-1}; **8**, 2273 cm^{-1}. Anal. Calcd for $C_{14}H_{21}N_7LaBr_3$: C, 25.26; H, 3.15. Found: C, 19.61; H, 2.55; $[CeBr_3(MeCN)_{4.7})]$.

■ RESULTS AND DISCUSSION

The $CeBr_3$/IL precursor paste (**1**) was used without further purification for the synthesis of $CeBr_3(THF)_4$ (**2**), $CeBr_3(2\text{-Me-THF})_4$ (**3**), and $CeBr_3(MeCN)_5 \cdot MeCN$ (**4**). A summary of the overall synthetic scheme is presented in Scheme 1. Large crops of colorless crystals of **2**−**4** suitable for X-ray were obtained from saturated solutions of **1** in their respective solvents at reduced temperature. Incorporation of the IL results in convenient access to substantial crystalline yields of these Ce compounds when compared to saturated solutions of bulk $CeBr_3$ alone (see the Experimental Section for compound **2**). The structure of **2** was confirmed by matching of the unit cell to the published structure of $CeBr_3(THF)_4$,[9] while the full data sets collected for **3** and **4** resulted in the 2-Me-THF and MeCN adducts of $CeBr_3$ depicted in Figures 1 and 2, respectively.

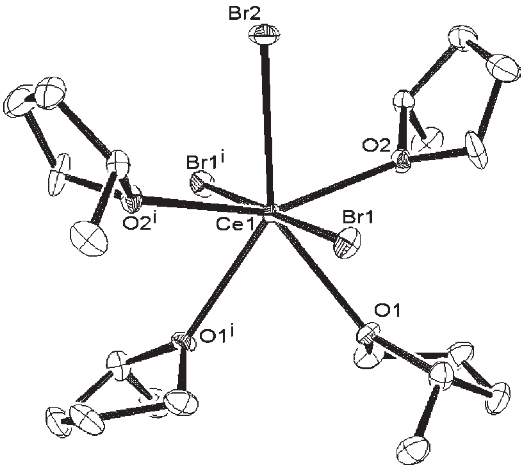


Figure 1. ORTEP view of **3** with thermal ellipsoids shown at 40% probability. All hydrogen atoms have been omitted for clarity.

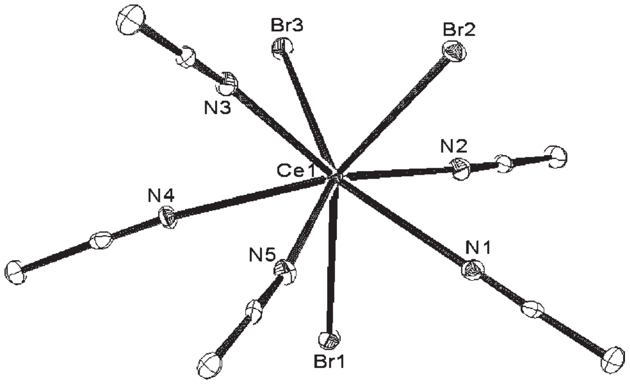


Figure 2. ORTEP view of **4** with thermal ellipsoids shown at 40% probability. All hydrogen atoms and lattice MeCN have been omitted for clarity.

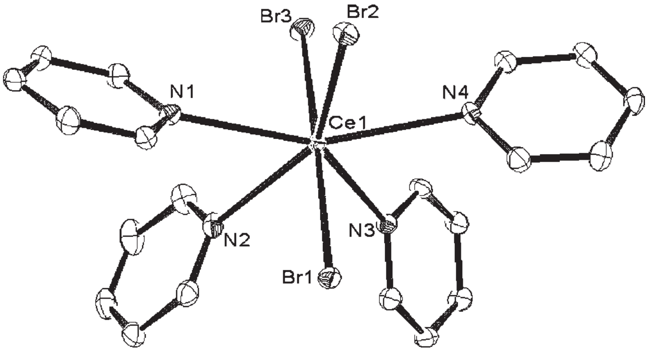


Figure 3. ORTEP view of **5** with thermal ellipsoids shown at 40% probability. All hydrogen atoms have been omitted for clarity.

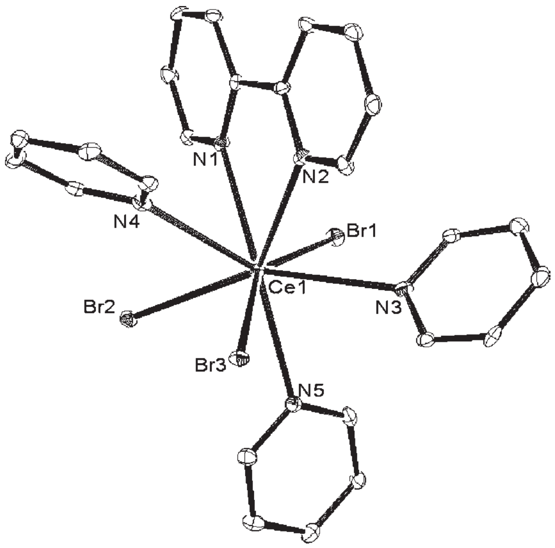


Figure 4. ORTEP view of **6** with thermal ellipsoids shown at 40% probability. All hydrogen atoms have been omitted for clarity.

The X-ray structures of **3** and **4** reveal the presence of four bound 2-Me-THF and five bound acetonitrile ligands, respectively. The higher coordination number observed for **4** can be explained by the diminished steric demands of the acetonitrile ligand relative to the bulkier tetrahydrofuran analogs of **2** and **3**. Structurally, both **3** and **4** are very similar to $CeI_3(THF)_4$, synthesized by Arnold and Liddle.[10] Interestingly, it was noted that addition of acetonitrile to **2** resulted in displacement of the THF solvating ligands, yielding a second synthetic pathway to **4**.

The observation that the solvating THF ligands in **2** are readily displaced by acetonitrile led to the assertion that **2** may serve as a suitable precursor for the synthesis of other ligated $CeBr_3$ adducts. Indeed, the reaction of **2** with pyridine results in, after work up, pure $CeBr_3(py)_4$ (**5**; Figure 3).

A second pyridyl adduct was obtained from the reaction of bipyridine and **2** in dichloromethane solution. Subsequent recrystallization from pyridine and hexanes led to the formation of $CeBr_3(bipy)(py)_3$ (**6**) as a yellow crystalline solid in good yield (Figure 4). Despite the presence of excess bipyridine in the reaction mixture, the crystal structure reveals the presence of a single bipyridine ligand bound to a $CeBr_3$ unit with the remaining coordination sphere being occupied by three pyridine ligands. Further emphasizing the synthetic utility of **2** is the observation that under identical reaction conditions, substitution of **2** with bulk $CeBr_3$ produces no apparent reaction.

The crystal data for **3**–**6** and **8** are presented in Table 1, and a selection of pertinent metrical parameters are provided in Table 2. The average Ce–Br bond distances for **3** and **5** of 2.895(5) and 2.881(4) Å, respectively, are similar to the value observed for $CeBr_3(THF)_4$ of 2.8940(9) Å.[9] In contrast, the analogous values observed for **4** and **6** of 2.9240(8) and 2.9403(7) Å, respectively, suggest a relatively enhanced electron density at the Ce(III) centers, resulting from the higher coordination number. Lastly, the average Ce–N bond distances for **5** and **6** are similar to values observed for related bonds in similar Ce(III) pyridyl systems.[11]

The presence of a single unpaired f-electron in the Ce(III) species somewhat limits the characterization techniques available for paramagnetic species **2**–**6**. Given the potentially labile nature of some of the solvating ligands of the Ce(III) adducts, it was of interest to synthesize representative examples of the corresponding diamagnetic La(III) adducts. Thus, crystals of $LaBr_3(THF)_4$ (**7**) and $LaBr_3(MeCN)_5 \cdot 2MeCN$ (**8**) were prepared by dissolution of bulk $LaBr_3$ in the respective hot solvents with subsequent cooling. The structure of **7** was confirmed by matching of the unit cell to the published structure,[12] while the identity of **8**

Table 1. Crystal Data for $CeBr_3(2\text{-}Me\text{-}THF)_4$ (3), $CeBr_3(MeCN)_5 \cdot MeCN$ (4), $CeBr_3(py)_4$ (5), $CeBr_3(bipy)(py)_3$ (6), and $LaBr_3(MeCN)_5 \cdot 2MeCN$ (8)

	3	4	5	6	8
empirical formula	$C_{20}H_{40}Br_3CeO_4$	$C_{12}H_{18}N_6CeBr_3$	$C_{20}H_{20}N_4CeBr_3$	$C_{25}H_{23}N_5CeBr_3$	$C_{14}H_{21}N_7LaBr_3$
M	724.37	626.17	696.25	773.33	666.02
T/K	140(1)	140(1)	140(1)	140(1)	140(1)
color	colorless	colorless	colorless	yellow	colorless
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	*C*2/*c*	$P2_1/n$	*Pbca*	*Cc*	$P2_12_12_1$
a/Å	22.421(9)	8.800(2)	17.1142(11)	16.770(4)	8.995(2)
b/Å	9.395(4)	13.250(3)	17.2768(11)	9.657(2)	12.433(3)
c/Å	16.657(11)	18.628(5)	32.582(2)	17.881(4)	21.698(5)
β/deg	131.149(3)	95.130(2)	90.0	115.304(2)	90.0
U/Å^3	2641.4(9)	2163.1(9)	9633.7(11)	2618.0(10)	2426.8(10)
Z	4	4	16	4	4
Dc/Mg m^{-3}	1.821	1.923	1.920	1.962	1.823
μ/mm^{-1}	6.281	7.65	6.879	6.341	6.710
cryst size/mm	0.28 × 0.26 × 0.12	0.35 × 0.24 × 0.24	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.18	0.16 × 0.14 × 0.04
reflns collected	13442	23229	90530	11606	23106
R(int)	0.0535	0.0363	0.0628	0.0297	0.0812
data/restraints/params	3106/13/140	5136/0/205	8954/0/505	4761/2/307	4411/0/233
absorption correction	semiempirical	semiempirical	semiempirical	semiempirical	semiempirical
R1 [$I > 2(I)$]	0.0359	0.0276	0.0330	0.0257	0.0510
wR2 (all data)	0.1411	0.1053	0.0762	0.0567	0.1216
largest peak, hole/e Å^{-3}	0.996, −1.202	1.066, −0.989	0.618, −0.657	0.625, −0.594	1.396, −1.893

Table 2. Selected Metrical Parameters (Å) for $CeBr_3(2\text{-}Me\text{-}THF)_4$ (3), $CeBr_3(MeCN)_5 \cdot MxeCN$ (4), $CeBr_3(py)_4$ (5), $CeBr_3(bipy)(py)_3$ (6), and $LaBr_3(MeCN)_5 \cdot 2MeCN$ (8)

bond	3	4	5	6	8
Ln−Br1	2.891(2) (i)	2.9513(8)	2.8902(6)	2.9460(7)	2.9592(6)
Ln−Br2	2.9044(14)	2.9261(8)	2.8833(6)	2.9226(8)	2.8967(6)
Ln−Br3		2.8945(7)	2.8687(6)	2.9524(7)	2.9505(7)
Ln−O1	2.544(3) (i)				
Ln−O2	2.518(3) (i)				
Ln−N1		2.657(4)	2.673(4)	2.632(4)	2.6839(5)
Ln−N2		2.626(4)	2.683(4)	2.605(4)	2.6960(4)
Ln−N3		2.643(4)	2.658(4)	2.778(5)	2.6790(5)
Ln−N4		2.647(4)	2.694(4)	2.865(5)	2.6626(5)
Ln−N5		2.639(4)		2.735(5)	2.6624(4)

was established on the basis of single-crystal X-ray diffraction (Figure 5). The addition of an internal standard (hexamethylbenzene) in ^1H NMR experiments demonstrated that while **7** retained the THF solvate molecules, **8** indicated a loss of lattice MeCN molecules resulting in a formula of $LaBr_3(MeCN)_{4.5}$. The elemental analysis (EA) data for **8** are in agreement with this result, indicating a composition of $LaBr_3(MeCN)_{4.7}$. In the case of the Ce(III) analog, the EA data indicate a significant loss of MeCN solvate molecules, resulting in the formula $CeBr_3(MeCN)_{2.8}$. This is further evidenced by the degradation of crystals of **4** to powder, also accompanied by a notable loss of mass. It is apparent that the MeCN adducts **4** and **8** are thermally unstable and readily desolvate over time at room temperature. This feature is also observed in **3**, with EA results yielding a formula of $CeBr_3(2\text{-}Me\text{-}THF)_{1.9}$. As with the MeCN adducts, desolvation is evidenced by the observation that clear, colorless blocks of **3** turn to chalk-like solids over the course of a few hours. It is of interest to note that the THF analogs of **2** and **7** both maintain their original crystalline structure over the course of weeks at ambient temperature. Thus, it is highly likely that the additional steric constraints imposed by the presence of the 2-Me groups in **3** account for the destabilization of the molecular adduct.

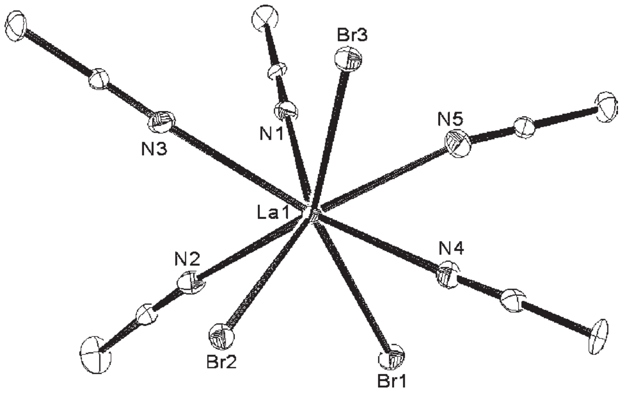


Figure 5. ORTEP view of **8** with thermal ellipsoids shown at 40% probability. All hydrogen atoms and two lattice MeCN solvent molecules have been omitted for clarity.

■ CONCLUSIONS

The addition of the IL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide to bulk $CeBr_3$ results in a precursor paste that significantly enhances $CeBr_3$ solubility in THF, 2-Me-THF, and MeCN relative to $CeBr_3$ and solvent alone.

Recrystallization from the respective solvents resulted in the formation of $CeBr_3(THF)_4$, $CeBr_3(2\text{-}Me\text{-}THF)_4$, and $CeBr_3(MeCN)_5 \cdot MeCN$. Furthermore, the THF adduct proved to be a suitable precursor for the synthesis of $CeBr_3(py)_4$ and $CeBr_3(bipy)(py)_3$. Lastly, both $LaBr_3(THF)_4$ and $LaBr_3(MeCN)_5 \cdot 2MeCN$ were independently prepared and characterized as diamagnetic analogs of their paramagnetic $CeBr_3$ counterparts. All new compounds were characterized by single crystal X-ray diffraction experiments and elemental analysis. The use of an IL to significantly increase isolable quantities of lanthanide halide solvates is expected to impact the fields of general organolanthanide chemistry as well as lanthanide containing materials chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data of complexes **3** (CCDC# 804894), **4** (804892), **5** (804895), **6** (804893), and **8** (804896) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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